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MÖSSBAUER EFFECT IN HEUSLER ALLOYS

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The Mössbauer absorption spectra of ternary alloys with the Cu_2MnAl type structure (Heusler alloys) were investigated. Tin Sn^{119} was used as the Mössbauer isotope. It was found that heat treatment affected the form of the Mössbauer spectra. The value of the internal magnetic field at the tin nuclei was determined for the compounds Co_2MnSn and Ni_2MnSn, in which it was found to be 42.0 and 70.5 kOe, respectively.

INTRODUCTION

IN 1898, Heusler discovered ferromagnetism in Mn–Sn alloys. Later, other ferromagnetic alloys, composed of nonferromagnetic elements, were discovered and investigated. In honor of the discoverer, these alloys are known as Heusler alloys. For ferromagnetism to appear in Heusler alloys, they must contain elements which are neighbors of iron in the periodic system.

The most interesting are the ternary Heusler alloys, in which two of the components are elements on the left and right of the ferromagnetic triad in the periodic table (for example, Cu_2MnAl and Cu_2MnSn). The electronic averaging in the d-band of metals, leading to configurations similar to the electronic configurations of ferromagnetic elements, has been put forward as an explanation of the ferromagnetism of such compounds. Many ternary compounds with Cu_2MnAl-type structure are known at present.[1-4] Some of these alloys contain elements of group VIII, while other have components which belong to groups VII-A and I-B. Some ternary compounds contain tin atoms, which can be used to investigate the Mössbauer effect using the Sn^{119} isotope.

In the present investigation, we studied the series of compounds listed in Table I. The numbers given in this table will be used to denote these compounds.

Of all the listed compounds, only Cu_2MnSn does not contain elements of the iron group and it is a classical representative of the Heusler alloys. All the other compounds include an element of group VIII but they are also of interest because the magnetic properties of these compounds have not yet been investigated at all and we hope that the present communication will stimulate further studies of these substances.

Heusler alloys have low Curie points $\Theta \sim 600$–$700\,^\circ$K, and low values of the saturation magnetization. The structure of the compound Cu_2MnSn changes when the temperature is varied; the low-temperature modification of this compound has a hexagonal unit cell with a disordered distribution of atoms, and belongs to the magnesium structure type, with the space group P6/mmc; the high-temperature modification is cubic, with the space

Table I

No.	Compound	System*	Lattice parameters		Reference
			a, Å	c, Å	
1	Co_2MnSn	cubic	5.99	—	[5-7]
2	Ni_2MnSn	cubic	6.05	—	[5-7]
3	Cu_2MnSn	cubic – ht	6.16	—	[8,9]
		hexagonal – lt	2.73	4.34	[10]
4	Cu_2FeSn	cubic – ht	5.92	—	[11]
		hexagonal – lt	2.73	4.34	[10]
5	Cu_2CoSn	cubic	5.97	—	[11]
6	Cu_2NiSn	cubic	5.91	—	[11]

*Notation: ht is the high-temperature phase; lt is the low temperature phase.

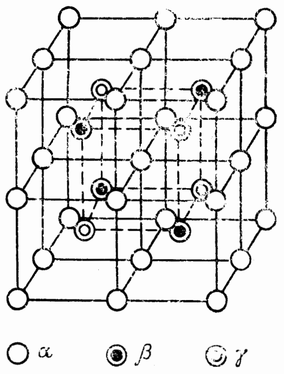

FIG. 1. Structure positions in the lattice of the Heusler alloys: the α position is occupied by atom A, the β position by atom B, and the γ position by atom C. A and B are metals of groups VII and VIII; C is tin.

group Fm3m. Table I presents data on the structure of the investigated compounds. The existence of two modifications has been established only for Cu_2MnSn and Cu_2FeSn.

The cubic modification, found in all compounds of the Cu_2MnAl type, has been investigated quite thoroughly; its structure is shown in Fig. 1. The crystal structure of this cubic modification has three positions: α, β, and γ. If the α position is occupied by an atom A, the β position by an atom B, and the γ position by an atom C, the structure formula may be expressed as A_2BC. In the first three compounds (Nos. 1–3 in Table I), the β and γ positions are occupied by manganese and tin atoms, while the α position is occupied by cobalt, nickel, or copper. The four compounds containing copper (Nos. 3–6) have a variable β position in which manganese is replaced in turn by one of the elements of the ferromagnetic triad.

Usually, compounds of the Cu_2MnAl type have a wide range of solubility, which is responsible for their concentration disorder. For example, some positions, occupied in the completely ordered state by B atoms only, may be occupied by A atoms when there is a departure from the stoichiometric composition, while under other conditions, the β and γ positions may exchange atoms. This is very important because the magnetic properties of these compounds depend strongly on the distribution of transition-metal atoms in the lattice sites. The range of existence of the cubic phase is known only for Cu_2MnSn. This compound changes gradually into the β-phase of the Cu–Sn system, i.e., it is related structurally to that system. It is well known[12] that the β-phase of the Cu–Sn system is an electronic compound and, therefore, there is sufficient justification to assume that the electron density plays an important role in the formation of the structure of the ternary compound Cu_2MnSn, and of other compounds of the same type.

1. PREPARATION OF SAMPLES AND METHOD OF INVESTIGATION

The easily fusible tin presented some difficulties in the preparation of the samples because the other two components had high melting points. In order to avoid a change in the alloy composition, synthesis was carried out in quartz ampoules in vacuum. The components were taken in the stoichiometric ratio, carefully mixed, and pressed. The charge was heated slowly until the components dissolved completely. Then, the alloys were subjected to a heat treatment. The single-phase structure of the samples was checked by an x-ray phase analysis and by a metallographic method. The x-ray analysis was carried out in cameras of the RKD-57 type, using iron radiation. Thermograms were recorded for a number of samples in order to analyze possible phase transitions with temperature. Only single-phase samples were used in the Mössbauer effect investigation.

The Mössbauer spectra were recorded using apparatus in which the absorber moved at a constant velocity. In these measurements, we used SnO_2 and Mg_2Sn sources.[13] All the data on the spectra given in the present paper were obtained using an Mg_2Sn source. This source and the absorbers were kept at 77°K. The absorbers had the same thickness with respect to tin (15 mg/cm^2) and were prepared from powders of alloys of beryllium dioxide. We investigated the Mössbauer spectra of all the samples using two heat treatments: a) quenching of the alloys after annealing for 20 hours at 800°C; b) annealing of the alloys for 20 hours at a temperature somewhat lower than 500°C, followed by slow cooling, together with the furnace, to room temperature.

2. RESULTS OF INVESTIGATION OF THE MÖSSBAUER SPECTRA

A. Annealed alloys. The Mössbauer spectra of four annealed alloys, Nos. 3–6, had a singlet line, similar to that shown in Fig. 2a for the compound Cu_2MnSn (No. 3). Two compounds, Co_2MnSn (No. 1; Fig. 2b) and Ni_2MnSn (No. 2; Fig. 2c), had a doublet structure in the Mössbauer line.

B. Quenched alloys. The Mössbauer spectra of the quenched alloys exhibited a singlet line in the case of samples Nos. 4–6. Because both the quenched and annealed alloys Nos. 4–6, Cu_2(Fe, Co, Ni)Sn, had a single line without singularities, we shall not consider them any further.

The other quenched samples exhibited a hyper-

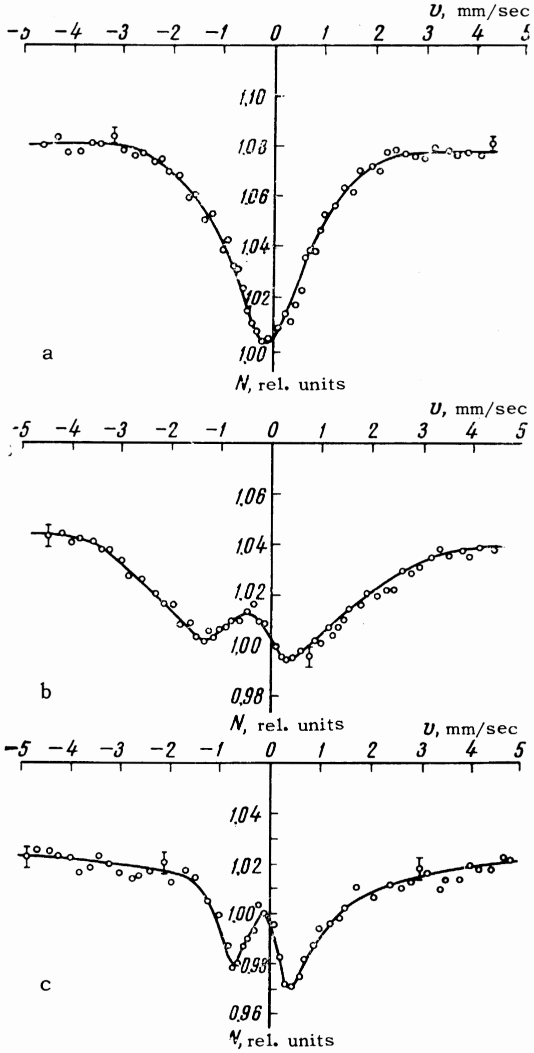

FIG. 2. Mössbauer spectra of the annealed alloys: a) Cu_2MnSn; b) Co_2MnSn; c) Ni_2MnSn.

fine structure in their Mössbauer spectra. The spectrum of the compound Cu_2MnSn consisted of nine resolved components (Fig. 3a). The spectra of the compounds Ni_2MnSn and Co_2MnSn, prepared using enriched tin, had almost the same hyperfine structure. Their spectra consisted of four components, exhibiting insufficiently resolved six-component Zeeman splitting. When the compound Co_2MnSn was prepared using enriched (to 65%) tin, we were able to observe the hyperfine structure of the normal Zeeman splitting into six components (Fig. 3b).

The Mössbauer spectrum of the compound Cu_2MnSn was more difficult to interpret because the form of the spectrum depended strongly on the heat treatment of the alloy. A sample of this alloy, rapidly cooled in air immediately after melting, exhibited a Mössbauer spectrum consisting of three lines (Fig. 4).

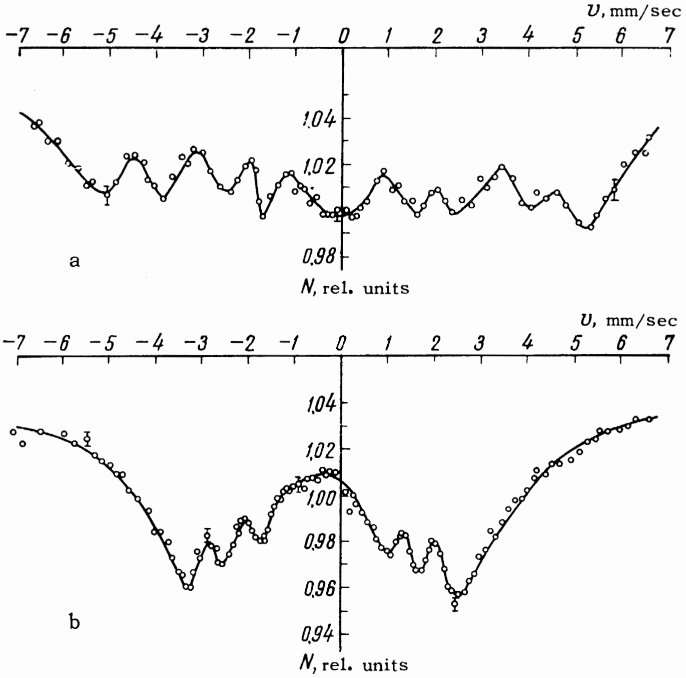

FIG. 3. Mössbauer spectra of the quenched alloys: a) Cu_2MnSn; b) Co_2MnSn.

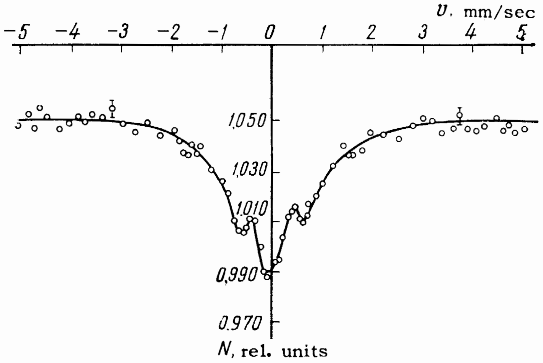

FIG. 4. Mössbauer spectrum of the alloy Cu_2MnSn rapidly cooled in air after melting.

C. Chemical shifts. The chemical shifts, determined from the positions of the lines in the Mössbauer spectra, differed little from one another. Heat treatment of an alloy had practically no effect on the value of the chemical shift. The difference between the values of the chemical shifts for the high- and low-temperature modifications was within the limits of experimental error. Table II lists the values of δ, measured relative to the Mg_2Sn source.

The shift δ increased monotonically in alloys Nos. 1–3 when elements of higher atomic number were substituted into the α position. In the case of alloys Nos. 3–6, when the metals in the β position were replaced, we found that the value of δ

Table II

Compound	δ, mm/sec		Compound	δ, mm/sec	
Co_2MnSn	−0.35	±0.02	Cu_2FeSn	+0.10	±0.02
Ni_2MnSn	−0.15		Cu_2CoSn	−0.08	
Cu_2MnSn	−0.10		Cu_2NiSn	−0.12	

was positive for the iron alloy (No. 4), but the values of δ for the remaining alloys in this group were practically unaffected.

3. DISCUSSION OF RESULTS

We shall consider first the annealed alloys. It is evident from Fig. 2 that the annealed alloys Co_2MnSn and Ni_2MnSn had the doublet line and the compound Cu_2MnSn had the singlet Mössbauer line. Our data on the thermal analysis showed that the first two compounds did not exhibit phase transitions of the first kind, while the compound Cu_2MnSn had a phase transition at ~500 °C. The low-temperature modification of Cu_2MnSn was hexagonal, while the structure of the compounds Co_2MnSn and Ni_2MnSn remained cubic both at high and low temperatures. It would seem that the singlet line should be observed in the compounds with the cubic structure. However, the random distribution of atoms in the hexagonal structure of the low-temperature modification of Cu_2MnSn probably destroys the axially-symmetric inhomogeneous electric field, and this gives rise to a single Mössbauer line.

The appearance of the quadrupole splitting in the Mössbauer spectra of the cubic crystals Co_2MnSn and Ni_2MnSn was unexpected. Before a detailed investigation is made of the magnetic properties of Heusler alloys, it is difficult to carry out a definitive analysis of the experimental data, but, bearing in mind Blume's investigation,[14] we can associate the appearance of a quadrupole with the magnetic properties of these compounds. According to Blume, the quadrupole asymmetry may be due to relaxation processes and magnetic field fluctuations, governed, to a considerable extent, by the immediate environment of the Mössbauer nucleus. In Heusler alloys, the environment of the Mössbauer nuclei depends very much on the heat treatment and, therefore, the investigated samples can be used to study the Blume effect.

It was easy to interpret the spectrum of the resonance absorption of γ quanta of the quenched alloy Co_2MnSn (Fig. 3b). The large magnitude of the effect made it possible to resolve clearly all six components of the spectrum, whose intensities represented an unpolarized absorber. Table III presents the data on the positions of the maxima of the components and on the types of transition.

Table III

No. of component	Position of maximum, mm/sec		Type of transition
1	−3.25	±0.05	+3/2 → +1/2
2	−2.50		+1/2 → +1/2
3	−1.70		−1/2 → +1/2
4	+1.05		+1/2 → −1/2
5	+1.75		−1/2 → −1/2
6	+2.50		−3/2 → −1/2

The separations between the components 1–2, 2–3, 4–5, 5–6 were, within the limits of experimental error, equal and, therefore, we could assume that there was no energy shift of the lines due to the quadrupole interaction. The values of the magnetic splitting of the ground and excited levels g_0 and g_1 were, respectively, 3.45 and 0.75 mm/sec. It is known that the ratio g_0/g_1 characterizes a given isotope and is independent of the value of the internal magnetic field at the nucleus—in our case, Sn^{119}. The value of $g_0/g_1 = 460$ obtained by us was in excellent agreement with the data of Kistner et al.,[15] who reported the value 4.64. Using the value of the magnetic moment of the ground state of the nucleus Sn^{119}, $\mu_0 = -1.0411 \pm 0.002$ n.m.,[16] we found $\mu = 0.68$ for the excited state, which again was very close to the value $\mu = 0.672$, reported in [15]. Our data on μ differed somewhat from those reported by Bryukhanov et al. (0.75),[17] Hanna et al. (0.78),[18] and Boyle et al.[19]

The internal magnetic field acting on the tin nuclei was found to be 42.0 kOe for the compound Co_2MnSn. Assuming that the compound Ni_2MnSn had the same splitting into six components as Co_2MnSn, we found H_{eff} in Ni_2MnSn was 70.5 kOe.

The most interesting was the Mössbauer spectrum obtained for the Cu_2MnSn alloy after quenching. In this case, the Mössbauer line was split into nine components (Fig. 3a) of almost equal intensity, instead of the six allowed by the splitting of the nuclear levels of Sn^{119} in a magnetic field. Careful preparation of the sample eliminated the possibility of a second phase and, therefore, the fine structure of the Mössbauer spectrum of the quenched sample of Cu_2MnSn had to be explained by features of its atomic structure. The possible disordered distribution of tin atoms in nonequivalent positions in the structure of this compound may be the cause of the departure of the spectrum from the normal form with six components.

A similar case is observed in the investigation of the Mössbauer spectra of the compound Fe_3Al,[20] which is a classical substance used in investigations of the ordering processes. If the structure formula of the compound Fe_3Al is represented in the form Fe_2FeAl, the structure of this compound becomes analogous to that of a Heusler alloy. In the Fe_3Al structure, there are two Fe positions: FeI has eight iron-atom neighbors and occupies the β position, while the nearest neighbors of FeII are four aluminum atoms and four FeI atoms and FeII occupies the α position. In the disordered state, the atoms of iron occupy equivalent positions and the Mössbauer spectrum has six components. In the ordered sample, the number of Mössbauer components increases and the spectrum then represents two superimposed six-component spectra.

Conversely, in the case of the compound Cu_2MnSn, six components are observed in the spectrum only in the ordered state, exactly as in the other two investigated compounds: Co_2MnSn and Ni_2MnSn. The presence of nine components in the Mössbauer spectrum of the compound Cu_2MnSn shows that quenching produces a partly ordered phase and that some tin atoms occupy the α and β positions instead of the γ positions. An estimate of the internal magnetic fields acting on the tin nuclei gives the value 76.0 kOe for the stronger field and 52.8 kOe for the weaker one. It is quite likely that the central maximum (Fig. 3a) has the same nature as the triplet obtained for the alloy rapidly cooled after melting (Fig. 4), in which such heat treatment probably produces two modifications: hexagonal and cubic, and the Mössbauer spectrum represents the sum of a single central line due to the hexagonal phase and a doublet due to the cubic phase. The degree of order of the Cu_2MnSn phase is difficult to estimate by x-ray diffraction because of the similar scattering capabilities of copper and manganese atoms. Therefore, the Mössbauer effect can be used in this case to investigate the distribution of atoms in the crystal structure and to find the ordering mechanism.

It is interesting to compare the data, obtained by other investigators, on the values of the effective magnetic fields for compounds of tin with elements from groups VII–VIII. Thus, Hanna et al.[18] reported Zeeman splitting in the chemical compounds Mn_4Sn and Mn_2Sn, which are ferromagnetic. For these compounds, H_{eff} were, respectively, 40 and 192 kOe; both these compounds are components of the ternary Cu–Mn–Sn alloys, which we investigated. Nikolaev et al.[21] investigated the antiferromagnetic compound $FeSn_2$; H_{eff} at the tin nuclei was found to be 25 kOe. The absorption spectra in both these investigations did not have sufficiently resolved hyperfine structure. Our data on the compound Co_2MnSn showed that the use of an Mg_2Sn source, having an emission line of natural width, and of an alloy containing enriched tin makes it possible to obtain a well-resolved spectrum.

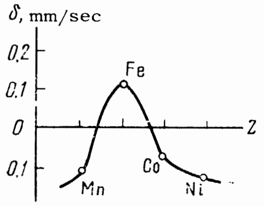

FIG. 5. Dependence $\delta \approx |\psi_s(0)|^2$ on the atomic number of the element Z.

It is worth drawing attention to the dependence of the chemical shift of samples Nos. 4–6 on the atomic number of the element in the β position (Fig. 5): the anomalous value of δ for sample No. 4 makes the curve in Fig. 5 similar to the well-known dependence of the exchange integral on the atomic number.

CONCLUSIONS

In considering the experimental data on the Mössbauer spectra of Heusler alloys, we find that the method of resonance absorption of γ quanta without recoil yields a wealth of information on the structure, properties, and phase transitions in these alloys. However, in some cases, the spectrum structure is complex so that quantitative results cannot be obtained. One can hope that when the investigation method is improved and, particularly, when the Mössbauer effect is used in conjunction with other methods, it will be possible to solve complex problems associated with the ordering of these alloys.

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